On the Magnetism of the Ferrites (La, Sr) FeO_x with Perovskite Structure

On the Magnetism of the Ferrites (La, Sr) FeO_x with Perovskite Structure*

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Synopsis

From X ray powder photograph of the solid solution of the system (Sr–La) FeO_x, it is revealed that the ferrite of the approximate composition 0.7 SrO 0.3 Fe_2O_3, which was reported to be cubic in the previous paper, has the structure closely related to perovskite. It is also found from thermomagnetic study that the susceptibility χ of strontium ferrite ($SrFeO_x$) is strongly dependent on thermal treatment, exhibiting anomalous behavior in $1/\chi - T$ curve. Quenched samples of $SrFeO_x$ seem to undergo an antiferromagnetic transition near 370°C, but the susceptibility increases with decreasing temperature below 200°C. Lanthanum ferrite ($LaFeO_3$) sintered at 1400°C is ferrimagnetic below 440°C, at which it undergoes a sharp magnetic transition, and above which it becomes paramagnetic. The Curie constants of both ferrites are abnormal, that of $SrFeO_x$ being smaller, whereas that of $LaFeO_3$ being greater than the value predicted for Fe^{3+} or Fe^{4+}. From the susceptibility data on the samples of various compositions of (Sr–La)FeO_x, it is suggested that some of the anomalous magnetic behaviors of these ferrites would be attributed to biassed occupation of Fe^{4+} ions in one of the non-equivalent sublattices caused by the lattice defects coming from O^{2-} deficiency.

I. Introduction

From the X ray study on the system of oxides SrO-Fe_2O_3, it was shown that the ferrite of the approximate composition 0.7 SrO 0.3 Fe_2O_3 was cubic, with the lattice constant $a = 3.86\,\text{Å} \times n$, n being an unknown integer[1]. The present study was carried out to know the crystal structure of this substance, and to correlate its magnetic property to the crystal structure. As will be described below, it has a structure closely related to perovskite, and its magnetic susceptibility shows, in many ways, abnormal features. Its ideal chemical formula should be designated as $SrFeO_3$, but the magnetic data obtained suggest that the lattice has a large number of oxygen (ion) defects, so that it is more appropriate to write the formula as $SrFeO_x$, where x is a number between 2.5 and 3. Hence, some of the ferric ions in this substance should be oxidized to tetravalent. In the present case, lanthanum ferrite ($LaFeO_3$) and its solid solution of $SrFeO_x$ have also been studied, with the aim of having a series of substances with continuously changing amount of Fe^{4+}, and hence, of deducing conclusions as to the magnetic behavior of this unfamiliar ion. Though the result has not been conclusive at present, due to the lack of quantitative analysis of that ion, some interesting informations were obtained on $LaFeO_3$, and the magnetic behavior of the system (Sr–La)FeO_x could be

* The 823rd report of the Research Institute for Iron, Steel and Other Metals.

(1) H. Watanabe, J. Jap. Inst. Met., **18** (1954), 588. (in Japanese)

considered to be an indication of the effect of Fe^{4+} ions.

In the course of this study, X ray study of a similar substance $BaFeO_x$ was reported by Okazaki *et al.*(2), and the electrical conductivity of the system $(La, Sr)FeO_x$ was measured by Jonker(3), and recently Yakel(4) made an extensive investigation on the structures of the perovskites including $SrFeO_x$ and $LaFeO_3$.

II. Samples and experimental procedure

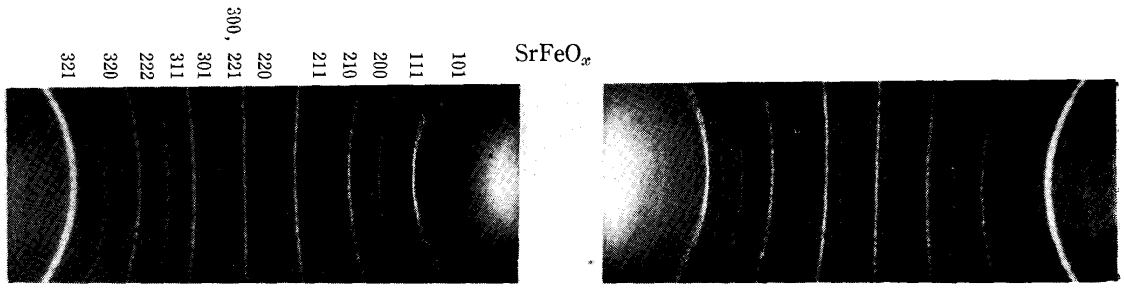
Samples of the oxides were made by the usual sintering process at temperatures ranging from 1,300 to 1,400°C. In general, high temperatures were utilized for ferrites containing large amount of lanthanum, since the high temperature susceptibility of these ferrites varied considerably with the sintering temperature, and the complicacy in the form of the inverse susceptibility vs. temperature curve appeared to be eliminated by utilizing high sintering temperatures. La_2O_3 used as a constitutional reagent contained Pr and Nd impurities not more than 1 per cent of the total mass, but in order to make sure of the reliability of the results, they were checked by iterating some of the experiments using La_2O_3 with the purity of more than 99.9 per cent. (containing 0.05 per cent of CeO_2 but neither Nd nor Pr being detected)

Magnetic measurements were made by a pendulum magnetometer, which could be used in the temperature ranges from −150°C to room temperature, and from room temperature to 900°C, separately. The scale value of this magnetometer was calibrated by measuring the susceptibility of nickel above its Cubic temperature. The rate at which the specimens were heated or cooled during the measurement of the susceptibility above room temperature was, in general, of the order of 200°C/h, except in the vicinity of the magnetic transition temperature of $LaFeO_3$ described below. Measurements of the susceptibility below room temperature were made exclusively by heating. The results of the measurements, in general, varied to some extent from sample to sample, and the curves given in this paper should be regarded as representative examples.

III. X ray study and the crystal structure

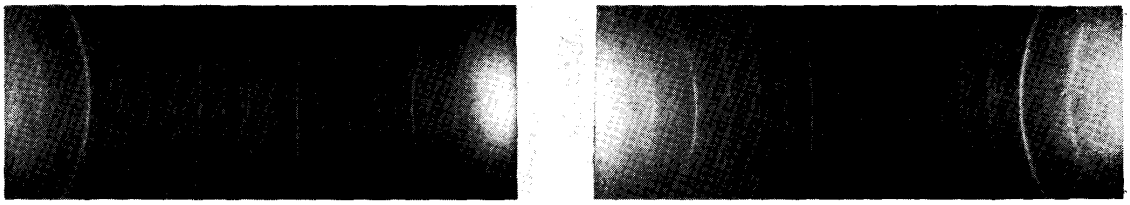
As was mentioned in **I**, $SrFeO_x$ has a cubic structure with the lattice constant $3.86 \times n$Å, n being an undetermined integer (Photo. 1). The lattice constant is nearly equal to those of the oxides grouped under the name of perovskites, and a comparison of the powder pattern with those of some perovskites suggested that it would have a very perovskite-like structure. To make sure of this supposition, powder patterns of nine samples of ferrites of the composition ranging from $SrFeO_x$ to $LaFeO_3$ were investigated, in order to see if the lattice constant of this series of oxides, which was expected to be a solid solution, really varied continuously with composition.

(2) Okazaki, Kubota and Mori, Nat. Techn. Rep., **1** (1955), 23.
(3) G. H. Jonker, Physica, **20** (1954), 1118.
(4) H. L. Yakel, Act. Cryst., **8** (1955), 594.



Phot. 1

$LaFeO_3$ sintered at 1400°C



Phot. 2

Lanthanum ferrite ($LaFeO_3$) has been reported by Náray-Szabó[5] and by Yakel[4] to be a perovskite. Contrary to expectation, a pattern distorted from cubic was obtained with a sample of lanthanum ferrit sintered at 1,400°C* (Photo. 2). Many lines were seen to be splitting in two, viz., (200), (210), (220), (221) or (300), (301), (311), (222), (320), (321), etc. At present, the reason for this discrepancy from the results of the previous authors is not obvious, but the difference in sintering temperature might be one of the reasons. No attempt has been made to determine crystal symmetry from the observed pattern. For the system (Sr-La) FeO_x, this splitting decreases gradually and vanishes at the composition near $La_{0.4}Sr_{0.6}FeO_3$.

If the stronger (220) lines are used to plot lattice constants against composition, assuming that the procedure of calculation in the case of cubic symmetry can be followed, Fig. 1 will be obtained, in which the lattice constant changes almost linearly with composition. It may be concluded, therefore, that $LaFeO_3$ and $SrFeO_x$ make a complete solid solution over the whole range of the compositions. The value of the lattice constant obtained for $LaFeO_3$, viz., 3.92 Å, is in good agreement with that obtained by Yakel (according to Yakel, $n = 2$, and so his lattice constant 7.852 Å is approximately twice as large as ours), though the coincidence might be fortuitous.

Since $SrFeO_x$ is of a perovskite-like structure, all of the ferric ions should be oxidized to tetravalent if, in an ideal case, x attains its maximum value 3. On the other hand, if no Fe^{4+} ion is formed, x will remain to be 2.5, and the crystal should contain a large number of oxygen defects. If the situation is intermediate

(5) Náray-Szabó, Naturw., **31** (1943), 466.

* The vessels used for sintering were SSA boats made by Nippon-Tôgyô Co. and no reaction between sample and vessel took place.

between the two extreme cases, x will take a value between 2.5 and 3. x has not been determined as yet in the present study, but the intensity of the line (110) in the X ray powder photograph suggests that x is not far from 2.5 for a sample quenched at 1,300°C. The quantitative evaluation should be made by chemical analysis.

IV. Results of the magnetic measurement

It is the general character of the oxides studied here that their magnetizations are strongly dependent on heat treatment. The essential factor of the heat treatment has been regarded, in the present experiment, as the cooling rate, though other factors such as oxidation during cooling, sintering atmosphere, etc. might also be of great importance. The present writer supposes that the origin of the non-reproducibility of the data often observed in the measurement of field dependence of magnetization should be attributed to such factors.

1. $SrFeO_x$

The inverse susceptibility vs. temperature curves are given in Figs. 1(a) and 1(b). The measuring field was about 6,000 Oe. There is a great difference between the curves of quenched samples and of slowly cooled ones. The quenching was done by cooling in air a small vessel containing about 1 g of the specimen, while the slow cooling was done by cooling the specimen at a rate not greater than 100°C/h. The curve for the quenched sample in Fig. 2 (a) was obtained during heating at a rate not so slow as to destroy the quenched character.

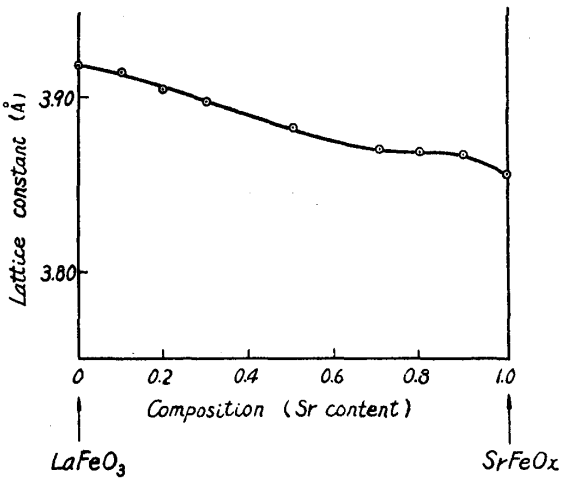


Fig. 1. Lattice constant vs. composition of the system (La, Sr)FeO_x computed from the position of (220) line, by the ordinary procedure of calculating lattice constants for cubic crystals.

At room temperature the magnetization of the slowly cooled sample is much greater than that of the quenched one. Both curves have peculiar features unfamiliar in the case of normal paramagnetism or antiferromagnetism. The curve of the quenched sample has an angular minimum at about 370°C. It was observed that the temperature of this anomaly remained unchanged, although the substance was cooled through it; hence, the nature of the transition may be regarded to be of electronic origin.

The corresponding anomaly in the curve of the slowly cooled sample is much less marked than that of the quenched one. The measurements at low temperatures indicate that this substance is neither ferromagnetic nor ferrimagnetic in the normal sense (Fig. 2(b)). Samples subjected to an intermediate rate of cooling naturally showed susceptibility curves running between those of quenched and slowly cooled ones, the anomaly at 370°C being smaller than that in the quenched one.

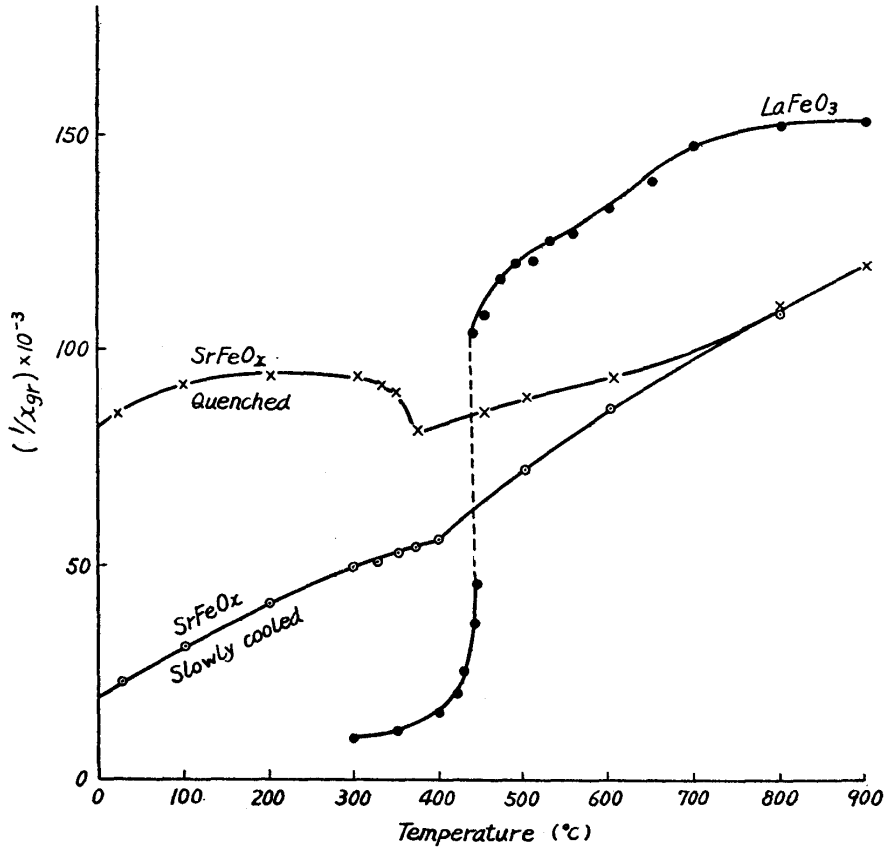


Fig. 2(a). Inverse mass susceptibility vs. temperature curves of $LaFeO_3$, quenched $SrFeO_x$, and slowly cooled one, above room temperature.

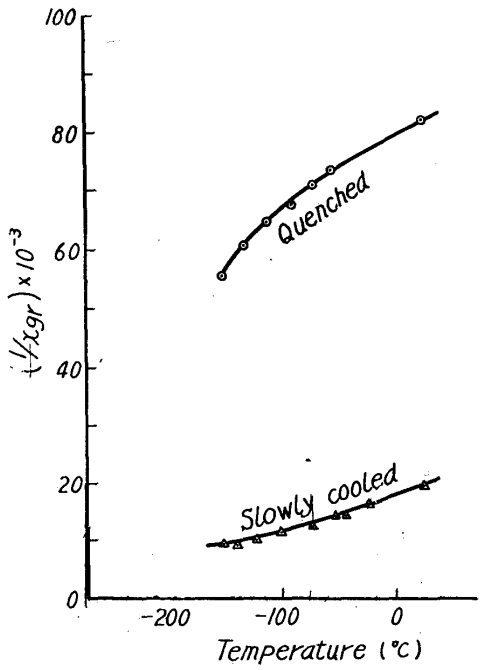


Fig. 2 (b). Inverse mass susceptibility vs. temperature curves of quenched $SrFeO_x$ and slowly cooled one, below room temperature.

Fig. 3 (a) shows an example of the field dependence of magnetization of a sample of $SrFeO_x$ at various temperatures. At a constant temperature, the magnetization varies linearly with magnetic field, but in general, the curve does not pass through the origin. The magnetization extrapolated to zero field is about 0.02 emu at most, which is smaller than the parasitic ferromagnetism found in a natural ferric oxide[6]. In Fig. 3 (b), similar data at room temperature for quenched and slowly cooled samples are shown. No sample of $SrFeO_x$ showed the saturation of magnetization below 7,000 Oe.

2. $LaFeO_3$

Inverse susceptibility vs. temperature curve and field dependence of magneti-

(6) L. Néel and R. Pauthenet, C. R., **234** (1952), 2172.

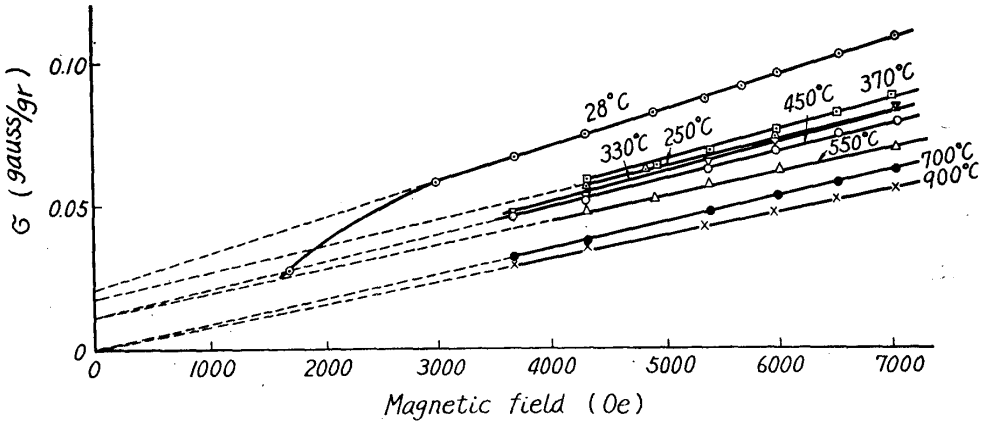


Fig. 3(a). Field dependence of magnetization of a sample of $SrFeO_x$ at various temperatures.

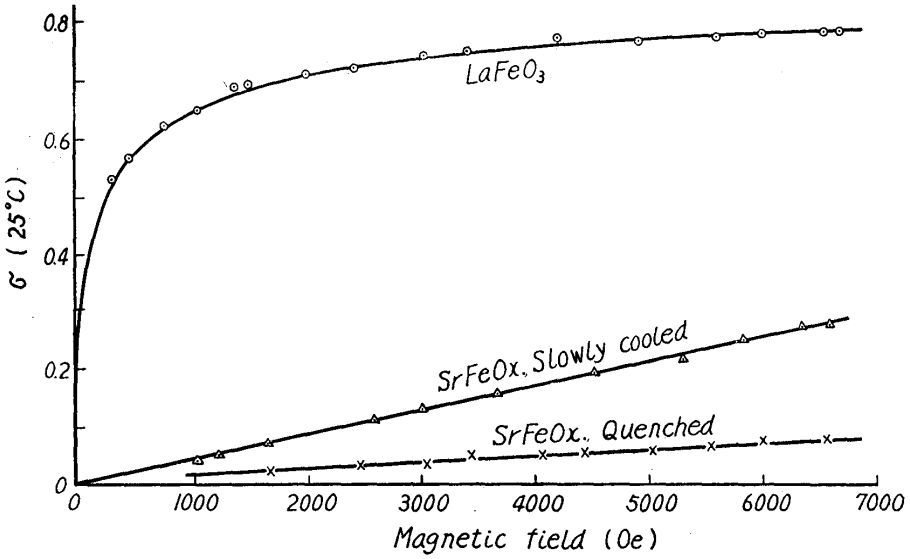


Fig. 3(b). Field dependence of magnetization of $LaFeO_3$, quenched $SrFeO_x$ and slowly cooled one, at room temperature.

zation of $LaFeO_3$ are given in Figs. 2(a) and 3(b). The curve in Fig. 2(a) was taken during the cooling of the sample at 900°C, which had been quenched at the sintering temperature 1,400°C. This transition is seen to be a first order transformation, which is characteristic of this substance, rather than the Curie temperature. The virtual Curie temperature seems to lie slightly above this transition point*. Below that temperature, the substance shows spontaneous magnetization, as can be seen from the curve of field dependence of magnetization in Fig. 3(b) and also from the magnetization vs. temperature curve in Fig. 4. The transition temperatures measured during heating and cooling coincide with each other, provided that the rate of change in temperature is sufficiently slow, but the susceptibility near the transition shows always some amounts of thermal hysteresis. On the higher temperature side, especially in the region from 440 to 700°C, the susceptibility measured during heating is greater than that measured during cooling, while on the lower temperature side, the situation is generally reversed**.

* G. Guiot-Guillain (C. R., **230** (1955), 1654) states that the Curie temperature of $LaFeO_3$ is 460°C.
** cf. G. Guiot-Guillain.

The effect of the sintering temperature will be given elsewhere.

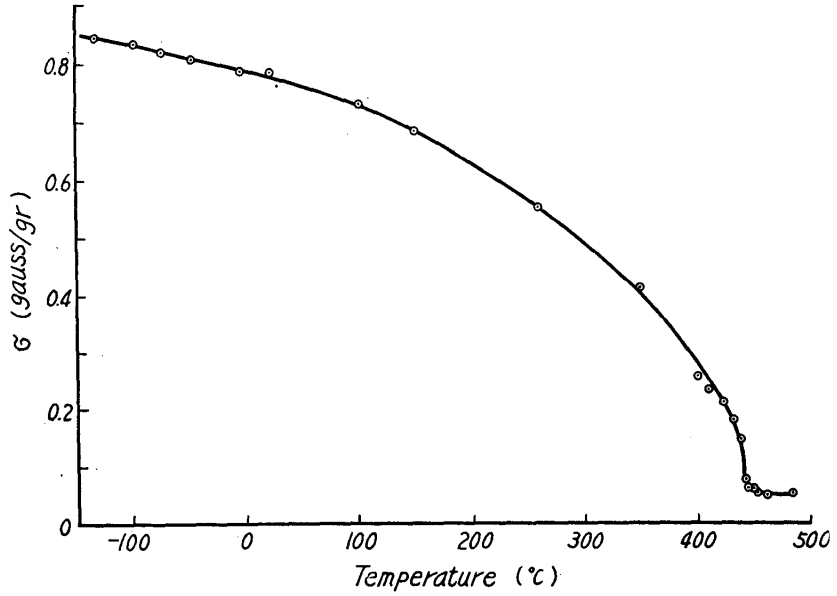


Fig. 4. Magnetization vs. temperature of $LaFeO_3$ at 6000 Oe.

3. (La, Sr)FeO_x

Interesting is the fact that the manner in which the susceptibility values change with addition of $LaFeO_3$ to $SrFeO_x$ is very similar to that obtained in $SrFeO_x$ by slowing the rate of cooling. Fig. 5 shows the inverse molar susceptibility vs. temperature curves of $La_{1-y}Sr_yFeO_x$ cooled at a constant rate at the sintering temperature. Comparing it with the curves in Fig. 2(a), it will be seen that the effect of decrease of y on the susceptibility is much the same as the change caused by decreasing the rate of cooling of the sample of $SrFeO_x$.

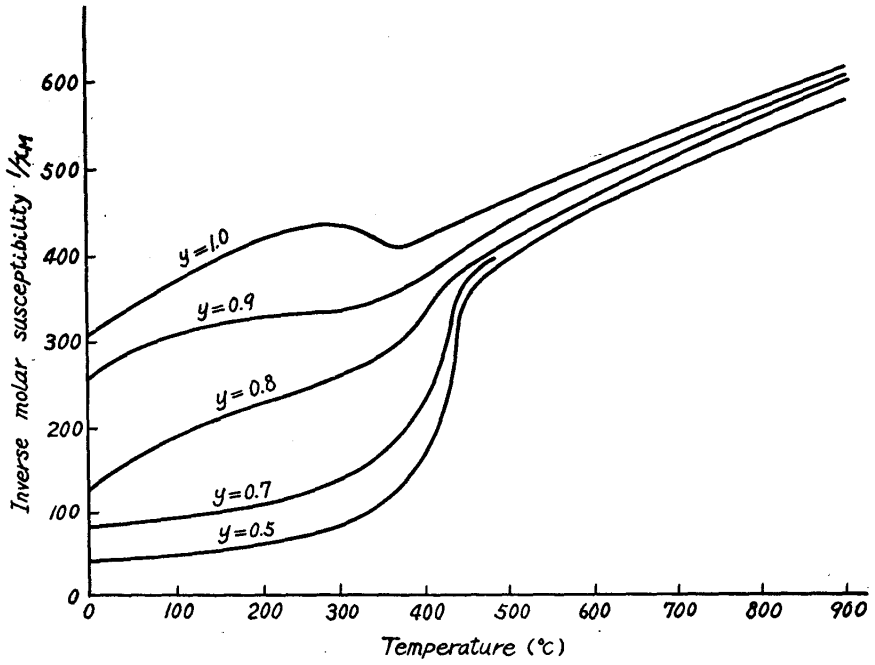


Fig. 5. Inverse molar susceptibility vs. temperature curves of $La_{1-y}Sr_yFeO_x$ cooled at a constant rate.

V. Discussion of the experimental results

Though, in the present study, $LaFeO_3$ has a distorted perovskite structure, which is in disaccordance with other authors', the conclusion that the whole of the system (La, Sr)FeO_x has perovskite-like structures is what has been expected from the foregoing studies. Hence, $SrFeO_x$ as well as those oxides containing lanthanum should have lattice defects of possessing Fe^{4+} on one hand, and of losing O^{2-} ions on the other. It is considered that such defects may play an important role in the anomalous behavior of magnetization exhibited by these oxides.

1. $SrFeO_x$

Since the effect of slow rate of cooling is to increase magnetization, it may be considered that, by such a treatment, the whole lattice will be divided into two unbalanced sublattices. In the case of quenching, the creation of the sublattices may be relaxed to lower temperatures. The mechanism of the creation of the unbalanced sublattices may be considered as follows: At high (sintering) temperatures, Fe^{4+} ions existing in the sample are very few, while O^{2-} defects are relatively numerous. If the sample is quenched at these temperatures, no ordering of O^{2-} defect can take place and, therefore, no formation of unbalanced sublattice. So the Fe^{4+} ions will be distributed at random among the lattice points. At a slow rate of cooling, on the contrary, some desects will be supplied by O^{2-} ions, the number of Fe^{4+} ions being increased, and there is sufficient time for the defects left behind to become ordered and, consequently, for the Fe^{4+} ions to go into a prefeiable sublattice.

The angular minimum at 370°C in the curve of the quenched sample may be regarded as the antiferromagnetic Curie temperature of the state without unbalanced sublattice. In contrast with the normal antiferromagnetics, the susceptibility value increases at temperatures below 200°C, which indicates the setting in of the delayed creation of unbalanced sublattices. It will be natural from the present consideration that this angular minimum should be almost faded out in the curve of the slowly cooled sample.

2. (Sr–La)FeO_x

Jonker states in his paper on the electrical conductivity of the system of (La,Sr)FeO_x that most Fe^{4+} ions are formed in the composition near $La_{0.5}Sr_{0.5}FeO_x$[3]. In the present magnetic measurements on the same system, the susceptibility increases as y decreases, that is La increases. This is in accordance with Jonker's picture, since the increase in Fe^{4+} may promote the unbalance of the created sublattices and hence, cause the increase of susceptibility values.

3. $LaFeO_3$

The temperature of magnetic transition, 440°C, can be regarded as that at which the creation or destruction of sublattices takes place. It is much sharper in this case than in the case of $SrFeO_x$. The mechanism of Fe^{4+} ordering might also be different from the case of $SrFeO_x$. Any conclusive statement, however, is impossible in the present stage.

The spontaneous magnetization per gram at low temperatures is about 0.85 emu. Hence, a magnetic ion in this substance has an average magnetic moment of $0.037\,\mu_\beta$. This value is of the same order of magnitude as the specific magnetization observed in a natural crystal of α-Fe_2O_3[6] ($\sim$0.5 emu in the direction of [111]). If this magnetization is caused by the biassed occupation of Fe^{4+} ions of one of the sublattices, the fraction of Fe^{4+} should be 3.7 per cent of the total magnetic ions. This estimation is consistent with Yakel's result[4] of 5 per cent from the chemical analysis.

4. Application of Elcock's theory to our experimental results

Elcock proposed a theory on ferri- and anti-ferromagnetism of substances containing lattice defects[7], which, though based, naturally, upon an idealized model, can reproduce qualitatively $1/\chi - T$ curves obtained here experimentally.

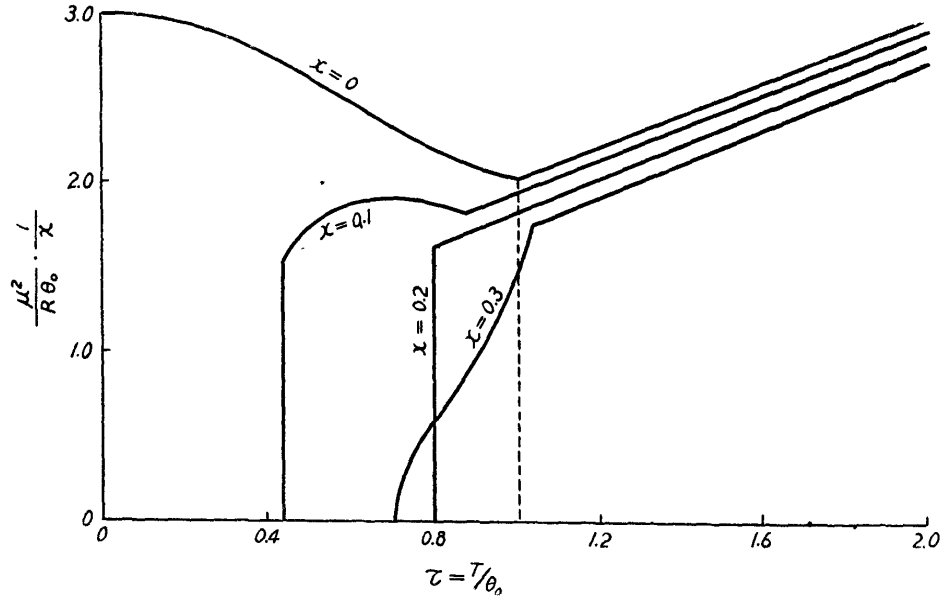


Fig. 6. Reduced inverse susceptibility vs. reduced temperature of non-stoechiometric compounds calculated theoretically by Eleock[9]. x: a parameter specifying the number of ions with excess valency over normal. χ: molecular susceptibility. θ: antiferromagnetic Curie temperature for $x=0$. μ: Bohr magneton. R: Gas constant.

His theoretical curves are given in Fig. 6, which correspond to various values of x, a measure of the number of ions with excess valency over normal, contained in a non-stoechiometric compound. In his theory, for small values of x, the temperature T_c of the creation of the unbalanced sublattices is lower than the antiferromagnetic Curie temperature θ ($x=0.1$ in the figure), while, for greater values of x, T_c becomes higher than θ ($x=0.3$ in the figure). There is a critical case in which T_c is equal to θ ($x=0.2$ in the figure). By comparing it with Fig. 2, it will be seen that quenched $SrFeO_x$, slowly cooled one, and $LaFeO_3$ correspond to $T_c<\theta$, $T_c>\theta$, and $T_c\fallingdotseq\theta$, respectively.

It may be noted, in conclusion, that the molar Curie constant of $SrFeO_x$ calculated from the magnetic measurements between 700 and 900°C is 1.83, which

(7) E. W. Elcock, Proc. Roy. Soc., **A227** (1954), 102.

is smaller than any of the spin-only values of Fe^{2+}, Fe^{3+} and Fe^{4+} (3.00; 4.38; 3.00, respectively). On the other hand, the corresponding value for $LaFeO_3$ is about 6.5, which is much higher than the spin-only values. The reason for this unexpected results is not comprehensible at present, and measurements at higher temperatures seem to be necessary.

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